

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/13304 A1

(51) International Patent Classification⁷: H01M 06/14

(21) International Application Number: PCT/US01/23495

(22) International Filing Date: 26 July 2001 (26.07.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/633,015 4 August 2000 (04.08.2000) US

(71) Applicant: SOUTHERN CLAY PRODUCTS, INC.
[US/US]; 1212 Church Street, Gonzales, TX 78629 (US).

(72) Inventors: GRUNEWALD, Frederick, A.; 2446 County
Grace, New Braunfels, TX 781310 (US). WALKER,
Donna; 37 Sesame Street, Toronto, Ontario M1W 2R3
(CA). NASESKI, Sasbo; 44 Brumwell Street, West Hill,
Ontario M1C 2K8 (CA).

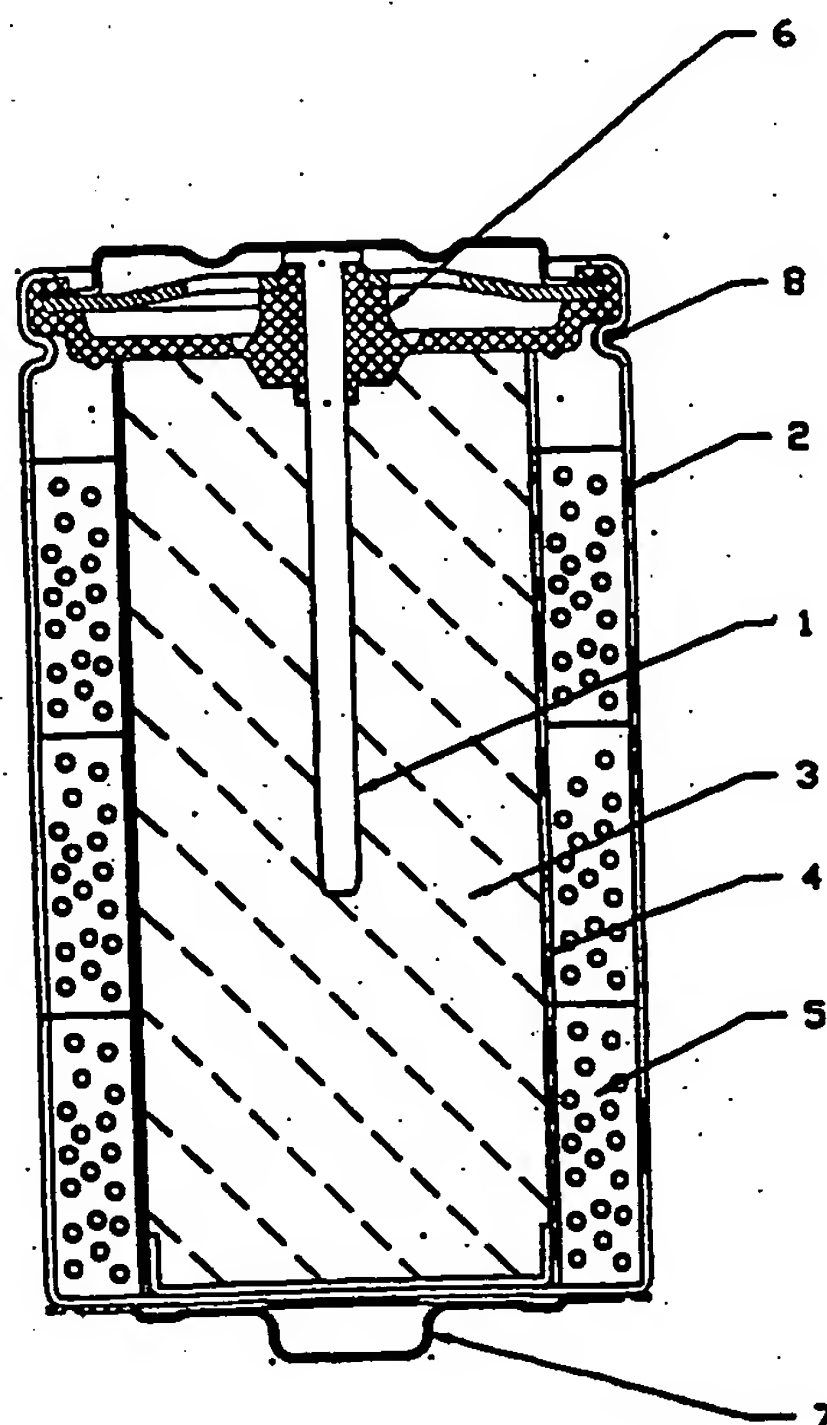
(74) Agent: WHEELER, George; McAndrews, Held &
Malloy, Ltd., Suite 3400, 500 West Madison, Chicago, IL
60661 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).

[Continued on next page]

(54) Title: GELLED ANODE OR ELECTROLYTE SOLUTION FOR AN ELECTROCHEMICAL CELL



(57) Abstract: A clay gelling agent produces an aqueous alkaline anode gel (3) with suspended metal particulate. The combination of clay with other non-clay gelling agents can produce a superior gelled anode, suitable for use in alkaline electrochemical cells. Furthermore, the addition of at least one starch gelling agent to a clay-based anode gel, a carboxyvinyl-based (i.e. CARBOPOL) anode gel, or a carboxymethylcellulose anode gel can produce a battery with improved stability when the cell is dropped, otherwise shaken, or exposed to heat. The present gelling agents can also be used to gel electrolyte solutions that do not contain suspended metal particles.

BEST AVAILABLE COPY

WO 02/13304 A1



Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE OF THE INVENTION

GELLED ANODE OR ELECTROLYTE
SOLUTION FOR AN ELECTROCHEMICAL CELL

FIELD OF THE INVENTION

The present invention relates to a novel gelling agent for use in gels for electrochemical systems, such as (but not limited to) anode gels and gelled electrolyte solutions for electrochemical cells.

BACKGROUND OF THE INVENTION

An electrochemical cell has a negative anode, a positive cathode and a separator between the two. The three components are wetted with an electrolyte solution that permits chemical reactions to take place at the electrodes. Although the technical definition of a battery is an array of two or more cells in one circuit, each cell is commonly referred to as a "battery." Any reference in this specification to a battery should therefore be understood to refer either to a single cell or to an array of two or more cells, as appropriate. A cell that contains an alkaline electrolyte is commonly referred to as an alkaline battery. Electrochemical cells are also classified as primary cells, which are disposed of after discharging them once, and rechargeable cells, which can be discharged, recharged, and discharged again.

For the cell to deliver useful electrical current, chemical reactions and diffusion must proceed at a sufficiently high rate. Metals, for example metal alloy powders, are commonly used for the electrodes. Metal alloy particles have a high surface area to volume ratios, effectively increasing the rate of reaction. The porosity of the electrodes must be appropriate for the electrolyte solution to provide for ionic diffusion and mass transport as well as allowing space for reaction products.

5 In the case of a typical manganese dioxide-zinc alkaline cell, the cathode is a pressed structure of manganese dioxide powder with graphite powder added for conductivity. The anode is commonly zinc-alloy powder suspended in an aqueous alkaline electrolyte solution such as potassium hydroxide solution. This mixture is gelled using one or more materials commonly referred to as "gelling agents." Selection of an anode gelling agent is important, as this choice will impact the ease or difficulty of battery assembly, electrical performance, cell stability, and hydrogen gas generation. Some of these cell assembly considerations (e.g. gel integrity and flow properties) are discussed by Bennett in 10 U.S. Pat. Nos. 5,686,204 and 6,040,088. Conventional gelling agents have included such materials as starches, gums and carboxymethylcellulose. U.S. Pat. No. 4,455,358 (Graham) describes an anode gel comprising a modified starch as the gelling agent. The applicant also cites U.S. Patent No. 6,022,639 (Urry) and U.S. Patent No. 3,936,318, (Cole, Jr.). Urry describes the use of 15 zinc flakes in an anode gel. Cole describes a two plate rechargeable cell.

Before 1991, electrical contact between the zinc particles and between zinc particles and the current collector were enhanced by the presence of a small amount of mercury amalgamated onto the zinc particles. The requirement to switch to mercury-free cells introduced problems of shock and vibration sensitivity, shelf life issues and "gassing" of the cells. Various changes in cell 20 design, gelling agents and/or corrosion inhibitors have been adopted since 1991 to overcome the shortcomings of mercury-free systems.

One such change was the switch from starch and carboxymethylcellulose gelling agents to a carbomer type gelling agent such as Carbopol®. Carbomers are now generally used by much of the industry, as they have proven to produce 25 anode gels of sufficient integrity and electrical performance. These systems, however, have still not overcome problems with shock and vibration stability. They also tend to have drawbacks in cell filling and equipment clean up, as the carbomer tends to make the gel sticky.

Much research work has been undertaken concerning the choice of gelling agents to overcome the problems of shelf life and sensitivity to shock during discharge of mercury-free alkaline manganese dioxide-zinc cells. U.S. Pat. Nos. 5,686,204 and 6,040,088 (Bennett) state that polyacrylate polymer made by modified bulk polymerization is a superior gelling agent in the anodes of alkaline electrochemical cells. The gels are said to resist syneresis (contraction of the gel accompanied by exudation of liquid). The gels also are said to provide lower viscosity, greater resistance to shock sensitivity, and superior electrical performance of the cells. U.S. Pat. No. 4,963,447 (Nishamura) also claims to overcome shock sensitivity in a alkaline cell by means of a granular crosslinking type branched polyacrylic or polymethacrylic acid gelling agent having a main particle diameter of 200 to 900 microns. The gelling agent is crosslinked in the presence of a mixture of a polyvalent allyl and vinyl crosslinking agents and then granulated.

In U.S. Pat. No. 5,587,254 (Kojima), shock resistance is said to be provided by the use of three gelling agents in combination, namely, (1) a crosslinked polyacrylate type with particle size mainly 100 to 900 microns, (2) a crosslinked and branched polyacrylic acid or salt thereof with particle size of mainly 100 microns or smaller and (3) a granular crosslinked and branched polyacrylic acid or salt thereof with particle size of mainly 100 to 900 microns.

BRIEF SUMMARY OF THE INVENTION

The present invention involves the use of at least one clay gelling agent or certain combined gelling agents for use in electrochemical systems, for example in an electrochemical cell. Although a commercially available type of alkaline cell is shown and described in detail in this specification and the drawings, the invention may be applied equally well to any cell containing a gelled component. The invention may be used without regard to size or shape (including, but not

limited to, sizes AA, AAA, C, D, and 9V), and without regard to the ingredients or form of the electrolyte, anode, and cathode.

One aspect of the invention is an electrochemical cell including a gelled anode suspension and a cathode. The gelled anode suspension contains anode metal particles, at least one clay gelling agent, and water. At least one non-clay gelling agent and other materials may optionally be used in the anode suspension as well.

A further aspect of the invention is the gelled anode suspension per se.

A still further aspect of the invention is a method of making an electrochemical cell comprising, in any order, providing a cathode, making a gelled anode suspension, and assembling the cathode and anode suspension in operative relation to form an electrochemical cell. The gelled anode suspension is made by combining the ingredients defined in this specification, typically including metal particles, at least one clay gelling agent, and water. Other ingredients may also be present.

Yet another aspect of the invention is an electrochemical cell comprising a cathode, an anode, and a gelled electrolyte suspension positioned in operative relation to each other to complete the cell. The gelled electrolyte suspension includes an electrolyte, at least one clay gelling agent and water. The ingredients of the gelled electrolyte suspension are present in amounts effective to form a gel.

Still another aspect of the invention is an electrochemical cell including a cathode and a gelled anode suspension. The suspension contains anode metal particles, at least one carboxyvinyl polymer (also known as "carbomer") or carboxymethylcellulose (CMC) gelling agent, at least one starch gelling agent, and water. Each ingredient is present in an amount effective to form a gel of the complete composition. The starch is present in an amount effective to improve the stability of the cell when dropped or heated. In addition, starch has been found to enhance cell electrical performance.

One or more of the following advantages may be realized, in whole or to some degree, by using the invention. The invention may reduce the cost of cell manufacturing, provide better electrical performance, or reduce the amount of the anode metal powder used (and thus the material cost of making the cell). The integrity of the gel may be improved and the suspension of the anode metal particles in the gel may be better maintained during manufacturing. The stability of the gel, particularly after the cell is stored or subjected to heat, may be improved. The batteries may be more stable and work better when subjected to mechanical shock or vibration, as by dropping or shaking them, either inadvertently or as part of the operation of a device powered by the batteries.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

Figure 1 is a longitudinal section of one embodiment of a cell for which the present invention can be used.

Figure 2 is a diagrammatic view of the time sequence of events in vibration tests carried out on a cell as described in the working examples.

Figure 3 is a diagrammatic view of how the cells were shaken in the vibration tests carried out in the working examples.

DETAILED DESCRIPTION OF THE INVENTION

While the invention will be described in connection with a limited number of embodiments, it will be understood that the invention is not limited to those embodiments. On the contrary, the invention includes all alternatives, modifications, and equivalents as may be included within the spirit and scope of the appended claims.

Referring to Fig. 1, a typically constructed alkaline cell includes a negative current collector or nail 1 and a positive current collector 2. The positive current collector or can 2 is an electrically conductive container open on one end and closed at the bottom. A gelled anode 3 is provided containing

metallic particles constituting the anode, suspended in an aqueous medium containing a gelling agent. The gelled anode can be made electrically conductive by adding an ionic electrolyte, such as potassium hydroxide. The ionic conductivity between the anode and the cathode can be provided by locating an aqueous potassium hydroxide electrolyte between the gelled anode and the cathode.

The gelled anode 3 is contained by and contacts a separator 4 and contacts the negative current collector 1. The separator 4 acts to pass ions but not electrons between the cathode and anode, thus preventing a short circuit in the cell. The lining or separator is generally a paper-like material which is sufficiently non-porous to prevent particles of the two electrode materials from passing through, yet absorbent and permeable enough to allow ions in an electrolyte to pass from one electrode material (the anode gel) to the other electrode material. Separators are described in U.S. Patent No. 5,674,639 (Urry).

Cathode annular rings 5 made of pressed manganese dioxide powder are inserted into the positive current collector 2, forming a pressure contact with the positive current collector 2. A sealing disk 6 supports and isolates the negative current collector 1 and defines a gas space for reaction gases. A terminal cap or central pip 7 serving as the positive terminal is welded onto the positive current collector 2. A bead 8 is rolled into the container 2 near the open end to support the sealing disk 6. The open end of the container 2 is crimped over the sealing disk 6, thus sealing the cell.

One example of the present invention is an improved alkaline battery or cell as shown in Figure 1, with the new anode gel as described below. In a conventional alkaline cell, the anode gel also contains an ionic electrolyte such as potassium hydroxide, which optionally can be part or all of the electrolyte of the cell. The anode and electrolyte of the present invention therefore can be provided as a single gelled slurry.

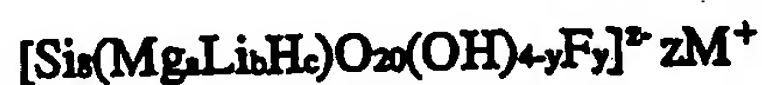
The present invention also is contemplated to find use for other types of electrochemical cells in which the anode is not provided in the form of particles suspended in the electrolyte gel. In this construction, the present invention can be used to gel the electrolyte solution.

5 The present invention also finds use in an alkaline cell in which part of the electrolyte solution is added to the cell after the cathode and separator are inserted, but prior to addition of the anode gel. This electrolyte solution is allowed to soak into the separator and cathode. Some of this electrolyte solution remains as a separate phase from the anode gel. In this cell construction, the
10 anode gel and the electrolyte solution function together as the electrolyte for the cell.

The clays that may be used as gelling agents may be natural, processed, or synthetic clays having gelling properties. The clays may be selected from smectite, attapulgite and sepiolite clays. Reference is made to Mineralogical
15 Society Monograph No.5, "Crystal Structures of Clay Minerals and their X-ray identification", Brindley, G. et al., 1980, for an identification of these clays and their constituent sub-groups. Processed clays are natural clays that have been processed to reduce impurities or to alter the balance of their constituents, for example by leaching or sedimentation or other techniques. Synthetic clays
20 having equivalent structures and having gelling ability may also be used. Synthetic clays may have the advantage of being made from pure materials, thus avoiding the presence of impurities that can cause gassing or other problems in some instances.

For example, the smectite mineral known as hectorite is a magnesium
25 silicate in which the anionic silicate lattice may or may not contain lithium and or fluorine atoms and is charge balanced by sodium or other cations. The hectorites useful here therefore include synthetic and natural minerals described in various terms in the prior art including sodium magnesium silicate, sodium magnesium fluorosilicate, sodium lithium magnesium silicate and sodium lithium

magnesium fluorosilicate. The preparation of synthetic hectorites by precipitation techniques is described in British Patent Nos. 1054111, 1213122 and US Patent No. 4049780 of Laporte Industries. Synthetic hectorite is available commercially under the trademark "Laponite" from Southern Clay Products, Inc. of Gonzales, Texas. Synthetic hectorite having a formula according to the following general empirical formula may suitably be used:



wherein $a = 4.95$ to 5.7 , $b = 0$ to 1.05 , $c = 0$ to 2 , $a+b+c = 4$ to 8 , $y = 0$ to 4 , $z = (12-2a-b-c)$ and M is Na^+ , Li^+ or another charge balancing cation.

The concentration of the clay is preferably at least 0.1% , suitably at least 0.025% by weight and effective to provide a gel having the required characteristics. The clay is not usually required to be in a concentration of more than 10% , more usually not more than 5% by weight in the gel. If synthetic clay, particularly synthetic hectorite, is used it may be possible to use a concentration of below 5% , even below 2.5% , by weight due to its high gelling ability.

The clay mineral is preferably present as at least about 10% by weight of the total gelling agents used, alternatively at least about 20% , at least about 30% , or up to 100% by weight of the total gelling agents used.

Preferably, one or more clay minerals, one or more synthetic clays, or a combination of mined and synthetic clays is used in conjunction with one or more non-clay gelling agents. "Non-clay" as used herein is broadly defined to include any gelling agent or adjunct that is not a smectite, attapulgite or sepiolite clay and that functions as a gelling agent or potentiates some other material as a gelling agent. Some examples of suitable non-clay gelling agents are a polysaccharide, for example, a polysaccharide gum, a modified or unmodified

starch, or a crosslinked acrylate polymer (e.g. a super absorbent polymer). Other non-clay gelling agents include carboxyvinyl polymers (e.g. carbomer type material such as Carbopol® brand carboxyvinyl polymer from BF Goodrich). Combinations of two or more non-clay gelling agents are also contemplated. The non-clay gelling agent is used to augment the properties of the clay gelling agent used in an electrochemical cell.

The polysaccharide gum non-clay gelling agent can be a xanthan gum (e.g. Kelzan® AR from Kelco Biopolymers). Preferably, the polysaccharide gum is used in at least 0.005% by weight in the gel and concentrations up to 1%, but more usually up to 0.5%, for example from 0.025% to 0.15% by weight are contemplated.

The non-clay gelling agent can be one or more starches, which may be modified starches or unmodified starches. For example, suitably, one or more starches selected from the group consisting of wheat, corn, waxy corn, potato, amilopectin potato, tapioca or a combination thereof can be used. Alternatively the starch may be a modified version of any of the above starches. The modification of the starch can be etherification including the formation of hydroxypropyl and hydroxyethyl ethers, esterification including acetylation, phosphating and other alkyl and inorganic treatments or crosslinking such as the formation of di-starch esters and di-starch ethers.

A particularly suitable starch is a potato starch such as Avebe® potato starch, sold by Cooperatieve Verkoop en Productievereniging van Aardappelmeel en Derivaten "AVEBE" B.A., a Netherlands corporation. If used in combination with a polysaccharide gum, in partial replacement thereof, starch further augments the properties of the gel in use in an electrochemical cell. Starch, a polysaccharide itself, can also be used in place of the polysaccharide gum. Syneresis can be controlled with just the starch. Preferably, the starch is used in at least 0.005%, preferably in at least 0.25% by

weight of the gel and concentrations of up to 1%, or even up to 2.5% by weight are contemplated.

5 The non-clay gelling agent can be a carboxyvinyl polymer (e.g. a carbomer such as Carbopol® 940 carboxyvinyl polymer from BF Goodrich) which can be used as from at least 0.005%, optionally at least 0.25% by weight of the composition. The carboxyvinyl polymer can be used as up to about 0.75%, alternatively up to 0.5% by weight of the composition. These proportions are representative, and do not represent mandatory limits. More or less than the stated proportions of any of the non-clay gelling agents can be used.

10 The non-clay gelling agent can be one or more crosslinked polyacrylate polymers, for example a sodium acrylate, potassium acrylate, ammonium acrylate polymer or a combination thereof. The cross-linked polymer may suitably be present in the gelling agent in at least 0.005%, suitably in at least 0.2% and up to 1% for example up to 0.4% by weight. The cross-linked polymer can be one or more super absorbent polymers such as, for example, Alcosorb® G1 from Ciba Specialty Chemicals to achieve the desired objectives. Various particle size distributions of the Alcosorb® material can be used with similar results.

15 The non-clay gelling agent that can be used in this invention can be carboxymethylcellulose, polyacrylamide, sodium polyacrylate, or other agents that are hydrolyzable in alkaline aqueous electrolyte solution.

20 The aqueous alkaline electrolyte can be an alkaline metal hydroxide such as sodium hydroxide, potassium hydroxide, and the like, or mixtures thereof. Potassium hydroxide is preferred.

25 The anode gel may contain the metal or metal alloy particulates defining the anode as at least 50% by weight, alternatively up to 80% by weight or more of the gel. These may be zinc metal or zinc alloy in powder, granules, flakes, combinations of these physical forms (any of which, as well as any other high-surface area to volume form of zinc, are defined for the present purposes as

“zinc particles”), or other physical forms of the metal. In one embodiment, zinc flakes can be present in an amount between about 5 percent by weight to about 70 percent by weight of the total zinc concentration, with the remainder being conventional zinc powder. Zinc particles having various particle size distributions can be used. After the desired anode particles are selected, the amount and selection of gelling agents and other ingredients can be optimized accordingly.

The zinc may be pure zinc, or an alloy comprising an appropriate amount of one or more of the metals selected from the group consisting of indium, lead, bismuth, lithium, calcium, aluminum, and the balance being zinc. Any combination of alloy compositions may be used for the powders and flakes. The anode gel further comprises at least sufficient water to function, and not so much water as to unduly dilute the gel or to cause the anode in suspension to settle out.

As a particularly preferred feature the present invention therefore provides an aqueous gel comprising one or more clay gelling agents; one or more non-clay gelling agents; optionally an electrolyte (to form an electrolyte gel or an anode gel); and optionally metal particulates (to form an anode gel); all as described and in the quantities indicated above.

Other components such as gassing inhibitors, organic or inorganic anticorrosive agents, binders, surfactants, conductive agents, or others, may be optionally added, simultaneously or separately, directly to the dry zinc mixture, or may alternatively be added to the electrolyte or gelled electrolyte before blending. Examples of gassing inhibitors or anticorrosive agents can include indium salts (such as indium hydroxide), perfluoroalkyl ammonium salts, alkali metal sulfides, etc. Examples of surfactants can include polyethylene oxide, polyoxyethylene alkyl ethers, perfluoroalkyl compounds, and the like. Apart from the gelling agent described in this specification, the primary cell components can be conventional. Electrochemical cells according to the present invention can be formulated, manufactured, and assembled by a person of

ordinary skill in the art without undue experimentation, based on the knowledge in the art and the present disclosure.

5 The gelling agents can be incorporated in an anode gel by dry blending a portion with the zinc powder, then dispersing the mixture in an aqueous electrolyte solution. They can also be incorporated directly in the electrolyte solution. Clumping can occur if the gelling agent is added directly as a dry powder to the electrolyte solution. Laponite should be hydrated in water, to achieve exfoliation, before adding the hydrated Laponite to the aqueous electrolyte solution. Skilled persons in this art do, however, know how to achieve adequate exfoliation when the Laponite is added dry to some formulas. 10 The order of addition and the methods of mixing the components are not critical to this invention, providing a useful product is formed.

Examples

15 The invention will now be illustrated by means of examples, which are not to be considered as exhaustive or restrictive of the scope of the invention. All compositions are by weight unless otherwise specified.

Example 1 (Control)

20 Standard cylindrical zinc/manganese dioxide alkaline AA size cells were prepared with a cathode active material, electrolyte solution and separator membrane. The cathodes contained 90% manganese dioxide, 6% graphite, and 4% 9N aqueous potassium hydroxide electrolyte solution. The separator membrane was an electrolyte permeable membrane of the non-woven polyvinyl alcohol (PVA)/rayon fiber type. The separator was wetted with 9N potassium 25 hydroxide free electrolyte solution containing 6% zinc oxide. The standard gelled zinc anode contained 65% zinc alloy powder, 33% potassium hydroxide electrolyte solution containing 6% zinc oxide, 0.5% Carbopol® C940 gelling agent, and the remainder being a metallic corrosion inhibitor of indium oxide.

The electrical performance of the cells was tested by continuously discharging the cells through 3.9 ohms and 1.0 ohm to a cut-off of 0.8 Volts. Table 1 shows the discharge capacity measured in ampere-hours ("Ah") at the specific cut-off voltage. A greater discharge capacity indicates a better cell, from the point of view of electrical capacity. The control cell showed a discharge capacity of 1.63 Ah on the 3.9-ohms test and 0.93 Ah on the 1-ohm test. For the experimental cells, Examples 2 to 9 provided below, the percent difference versus the control cells with the Carbopol[®] gelling agent is shown.

A drop test and a vibration test were also performed on the cells. The drop test is designed to measure the cell sensitivity due to mechanical shock. This mechanical shock is provided by dropping the cells from a height of 1 meter onto a steel plate mounted on a concrete base. Each cell was dropped three times, once onto the positive end, once onto the negative end, and once onto a side. The amperage of each cell was measured prior to the first drop and immediately after the third drop. The results are presented as the percentage of the initial amperage less 100% (i.e. percent difference). The smaller the difference between amperages the more stable the cell is. The result for the control cell is seen in Table 1 indicating an -8 % difference.

In the vibration test, two cells in series were mounted on a test board and subjected to three different vibration environments: vertical impact, horizontal impact and vibration in two horizontal directions. This test simulates a motorized toy race car requiring two AA cells, running on an assembled racecar track with track variations that lead to three-dimensional forces.

The three vibration environments are: (1) Vertical Impact (D0) - The cells were mounted in a cell holder and hit with a 60 pound per square inch vertical impact by a 1/2 inch cylindrical hammer mounted on a pneumatic piston. This vertical impact was applied every 6 seconds for a total of 10 strokes/minute. (2) Horizontal Impact (D1) - The test board, which had the cell holders mounted to it, was hit horizontally by a pneumatic piston in intervals of 5 seconds on and 5

seconds off. (3) Vibration (D2) - A pneumatic turbine was mounted underneath the test board which had the cells mounted to it. This turbine vibrated vigorously for 55 seconds/minute.

Figure 2 shows the sequence of events from D0-D2 and the time in seconds, while Figure 3 shows the motion of the cell during each vibration environment.

Vibration tests are measured by service time to a certain cutoff voltage. The maximum service time was set to 60 minutes. If the cell voltage exceeded the cutoff voltage after 60 minutes, the final cell voltage was reported. Thus, if the cell lasted for 60 minutes without falling below the cutoff voltage, the higher the final voltage, the better the result.

Table 1 shows that the service time for this control example was over 60 minutes at a cut-off voltage of 0.85V.

Example 2

AA alkaline cells as in Example 1 were prepared, but with 1.8% Laponite® JS (from Southern Clay Products, Inc.) synthetic clay mineral in place of the Carbopol® C940 gelling agent referenced above. The water normally used to dilute concentrated potassium hydroxide for the 9N anode electrolyte solution was used to prepare an 18% Laponite JS solution premix. The Laponite was mixed with the water until hydration was complete and then the solution was used to prepare the anode gel. The electrolyte solution concentration was adjusted to accommodate for use of the water in the premix as well as the higher concentration of Laponite® JS used to prepare the gel (versus the Carbopol® control).

The experimental cells were made one day after the anode gel was prepared.

The performance and drop test results for the experimental cells are noted in Table 1, where the experimental cells exhibited lower performance in the 3.9-ohms and 1.0-ohm tests: -13.7% and -15.8% respectively. In addition, the drop

test showed a -60% difference in drop, indicating an unstable gel. In the vibration test, the Laponite® JS cells failed after 2 minutes.

The anode gel of Example 2 showed syneresis after one day. This syneresis has the disadvantage that the anode gel would need to be used immediately after it is made. For optimal commercial manufacturing, the gel preferably should remain gelled without substantial syneresis for at least three days, so it can be made several days before it is used to fill cells.

Example 3

In this example, a non-clay gelling agent was used with the clay gelling agent to prevent syneresis from occurring. The non-clay gelling agent used was a polysaccharide gum (Kelzan® AR xanthan gum from Kelco Biopolymers). This produced a stabilized gel for up to a week.

The same AA alkaline cells as in Example 2 were prepared but with 0.75% Laponite® JS and 0.3% Kelzan® AR. The amount of electrolyte was adjusted to accommodate the addition of Kelzan® AR. Experimental cells were made three days after the anode gel was prepared.

The electrical performance as well as drop and vibration stability of the experimental cells is noted in Table 1. The experimental cells exhibited similar performance to the control at 3.9 ohms and a slightly higher performance, +16.8%, at 1 ohm. In addition, the drop test showed performance similar to the control.

In the vibration test, the addition of Kelzan® AR increased the service time to 28 minutes, after which the cells failed (0V).

Example 4

In evaluating various additions of non-clay gelling agents, it was noted that the addition of starch significantly improved the drop test and performance at 3.9 ohms and 1.0 ohm.

The same AA alkaline cells as in Example 3, were prepared but with 0.5% Laponite® JS, 0.1% Kelzan® AR, and 0.75% potato starch (Avebe® potato starch). The concentration of the electrolyte solution was adjusted to accommodate the addition of starch. Experimental cells were prepared three days after making the anode gel.

The results for electrical performance as well as drop and vibration stability are noted in Table 1. The experimental cells exhibited a slight increase in performance at 3.9 ohms (+4.0%) and a +27% increase at 1.0 ohm. In addition, the experimental cells showed excellent drop results, indicating a very stable, distributed zinc network.

With the addition of starch, the cells lasted over 60 minutes in the vibration test; however, the cell voltage showed large fluctuations.

Example 5

Although the above experimental cells passed the vibration test, another non-clay gelling agent was noted to improve gel stability during vibration. This non-clay gelling agent was a crosslinked polyacrylate super absorbent polymer provided by Ciba Specialty Chemicals under the trademark Alcosorb® G1.

The same AA alkaline cells as in Example 4 were prepared but with 0.5% Laponite® JS, 0.1% Kelzan® AR, 0.5% potato starch, and 0.25% Alcosorb® G1. The level of starch was adjusted to accommodate the addition of the Alcosorb® G1.

The results for electrical performance as well as drop and vibration stability are noted in Table 1. The experimental cells exhibited similar performance to the control at 3.9 ohms (-3.4%) and at 1.0 ohm (0%) with the drop results comparable to the experimental cells of Example 4.

In the vibration test, the cells lasted over 60 minutes at a cut-off voltage of 0.87V. The slightly higher cutoff voltage in comparison to the control cells of Example 1 indicates that these cells will run longer than the control cells.

Example 6

The major cost contributor to the anode gel system is the zinc alloy particulate or powder. In this experiment, the zinc alloy powder was reduced to 64% from 65% to see if the same electrical performance is maintained. This decrease would reduce the cost of the anode gel by approximately 1.5%. In addition, to further reduce costs of this system, the starch was decreased to 0.25% from 0.50% to see if drop test performance equivalent to the Carbopol control anode gelling system (Example 1) could be achieved.

Thus, the same AA alkaline cells as in Example 5 were prepared but with 64% zinc and 0.25% potato starch. The concentration of the Laponite solution was decreased to balance the loss of zinc and starch in the anode gel system.

The performance, drop, and vibration results are noted in Table 1. The performance of the experimental cells shows a very slight decrease in performance at 3.9 ohms, compared to Example 1, but a slight increase compared to the equivalent Laponite JS anode system of Example 5. Performance at 1.0 ohm was actually 15% higher when compared to both Example 1 and Example 5.

The drop test results showed equivalent drop performance to Example 1 but poorer performance in comparison to Example 5, due to the lower levels of potato starch used.

In the vibration test, the cells lasted over 60 minutes to a cut-off voltage of 0.88V, indicating that these cells will run longer than the control cells.

Examples 7-9

These examples were carried out similarly to Examples 2-6, but natural clay gelling agents were used instead of LAPONITE® synthetic clay. Performance was comparable on 3.9 ohms to the CARBOPOL control and slightly lower on 1.0ohm. Good drop performance was seen. The results of Examples 7-9 are presented in Table II.

Table I:

Example No.	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Gel Agent wt.%, identity	0.5 Carbopol ® C940 non-clay gellant	1.8 Laponite ® JS Synthetic clay gellant	0.75 Laponite 0.3 Kelzan non-clay gellant	0.5 Laponite 0.1 Kelzan, 0.75 Starch non-clay gellant	0.5 Laponite, 0.1 Kelzan, 0.5 Starch, 0.25 Alcosorb non-clay gellant	0.5 Laponite , 0.1 Kelzan, 0.25 Starch, 0.25 Alcosor b
Zn Powder % in Anode	65.16	65	65	65	65	64
Tests:						
3.9 ohms continuous discharge to 0.8V Capacity in Ah	1.75	1.51	1.76	1.8	1.69	1.71
% vs. Example 10 (Control)	0	-13.7 %	+0.6 %	+2.9 %	-3.4 %	-2.3 %
1.0 ohms continuous discharge to 0.8V Capacity in Ah	0.95	0.8	1.11	1.21	0.95	1.1
% vs. Example 10 (Control)	0	-15.8	16.8	27.4	0.0	15.8
Drop Test:						
Initial Amps	8.79	3.12	10.36	9.06	9.07	10.94
Post Amps	8.13	1.24	9.55	9.48	9.69	10.17
% change	-8	-60	-8	5	7	-7
Vibration Test:						
Service Time in minutes (at cut-off voltage)	over 60 (0.85V)	2 (0V)	28 (0V)	over 60 (0.9V)	over 60 (0.87V)	over 60 (0.88V)

Table 2

Example No.	Example 7	Example 8	Example 9
Gel Agent %, Identity	0.5 Natural Clay (Mineral Colloid MO), 0.1 Kelzan, 0.25 Starch, 0.25 Alcosorb	0.5 Attagel 50 Natural Clay, 0.1 Kelzan, 0.25 Starch, 0.25 Alcosorb	0.5 Pangel S-9 Natural Clay, 0.1 Kelzan, 0.25 Starch, 0.25 Alcosorb
Zn Powder % to Anode	65	65	65
Tests:			
3.9 ohms continuous discharge to 0.8V Capacity in Ah % vs Example 1 (Control)	1.72 -1.7	1.75 0.0	1.8 2.9
1.0 ohms continuous discharge to 0.8V Capacity in Ah % vs Example 1 (Control)	0.87 -8.4	0.88 -7.4	0.84 -11.6
Drop Test:			
Initial Amps	5.87	5.41	5.48
Post Amps	6.09	5.31	5.11
% change	4	-2	-7
Vibration Test:			
Service Time in minutes (at cut-off voltage)	over 60 (0.85V)	over 60 (0.87V)	over 60 (0.88V)

CLAIMS

1. An electrochemical cell comprising
a gelled anode suspension comprising anode metal particles, at
least one clay gelling agent, and water, each present in an amount
effective to form a gel; and
a cathode.
2. The electrochemical cell of claim 1 wherein said anode metal is at
least one zinc or zinc alloy particulate.
3. The electrochemical cell of claim 1 wherein said clay gelling agent
comprises at least one naturally occurring, refined or synthetic mineral selected
from attapulgite, sepiolite, or smectite.
4. The electrochemical cell of claim 1 wherein said clay gelling agent
comprises one or more of naturally occurring, refined, or synthetic smectite.
5. The electrochemical cell of claim 1 wherein said clay gelling agent
comprises natural hectorite
6. The electrochemical cell of claim 1 wherein said clay gelling agent
comprises synthetic hectorite
7. The electrochemical cell of claim 1 wherein said clay gelling agent
comprises synthetic hydrous sodium magnesium silicate.
8. The electrochemical cell of claim 1 wherein said clay gelling agent
comprises synthetic hydrous sodium lithium magnesium fluorosilicate

9. The electrochemical cell of claim 1 wherein said clay gelling agent comprises synthetic hydrous sodium lithium magnesium silicate.

10. The electrochemical cell of claim 1 wherein said clay gelling agent comprises synthetic hydrous sodium lithium magnesium fluorosilicate.

5 11. The electrochemical cell of claim 1 wherein said anode gel further comprises at least one non-clay gelling agent.

10 12. The electrochemical cell of claim 11 wherein said non-clay gelling agent is selected from the group consisting of polysaccharides, carboxyvinyl polymers, crosslinked polyacrylate polymers and combinations thereof.

13. The electrochemical cell of claim 11 wherein said non-clay gelling agent is xanthan gum.

15 14. The electrochemical cell of claim 11 wherein said non-clay gelling agent is at least one polysaccharide present at between about 0.005% and about 1% of the total weight of the anode gel.

20 15. The electrochemical cell of claim 11 wherein said non-clay gelling agent is at least one carboxyvinyl polymer present at between about 0.005% and about 0.75% of the total weight of the anode gel.

25 16. The electrochemical cell of claim 11 wherein said non-clay gelling agent is at least one crosslinked polyacrylate polymer.

17. The electrochemical cell of claim 16 wherein said crosslinked polyacrylate polymer is selected from the group consisting of sodium acrylate, potassium acrylate, ammonium acrylate or a combination thereof.

18. The electrochemical cell of claim 16 wherein said crosslinked polyacrylate polymer is present at between about 0.005% and about 1% of the total weight of the anode gel.

5 19. The electrochemical cell of claim 11 wherein said non-clay gelling agent is at least one unmodified or modified starch.

20. The electrochemical cell of claim 19 wherein said starch is present at between about 0.005% and about 2.5% of the total weight of the anode gel.

10 21. The electrochemical cell of claim 19 wherein said starch is present at between about 0.25% and about 1% by weight of the total weight of the anode gel.

15 22. The electrochemical cell of claim 1, wherein said anode comprises zinc and said cathode comprises manganese dioxide.

23. The electrochemical cell of claim 22, wherein said gelled anode suspension further comprises at least one alkaline electrolyte.

20 24. A composition comprising:
anode metal particles;
a clay gelling agent; and
water;
25 present in amounts effective to form a gel.

25. A method of making an electrochemical cell comprising, in any order:

a. providing a cathode;

b. making a gelled anode suspension by combining anode metal particles, at least one clay gelling agent, and water in amounts effective to form a gel; and

c. assembling said cathode and said gelled anode suspension in operative relation to form an electrochemical cell.

26. An electrochemical cell comprising

a. an anode;

b. a cathode; and

c. a gelled electrolyte suspension positioned in operative relation to said anode and said cathode, said gelled electrolyte suspension comprising at least one electrolyte, at least one clay gelling agent, and water, each present in an amount effective to form a gel.

27. An electrochemical cell comprising

a. a gelled anode suspension comprising anode metal particles, at least one first gelling agent selected from carboxyvinyl polymer and carboxymethylcellulose, at least one starch second gelling agent, and water, each present in an amount effective to form a gel, and the starch present in an amount effective to improve the stability of the cell when dropped or heated or both; and

b. a cathode.

28. The electrochemical cell of claim 27, wherein said first gelling agent comprises carboxyvinyl polymer.

29. The electrochemical cell of claim 27, wherein said first gelling agent comprises carboxymethylcellulose.

1/3

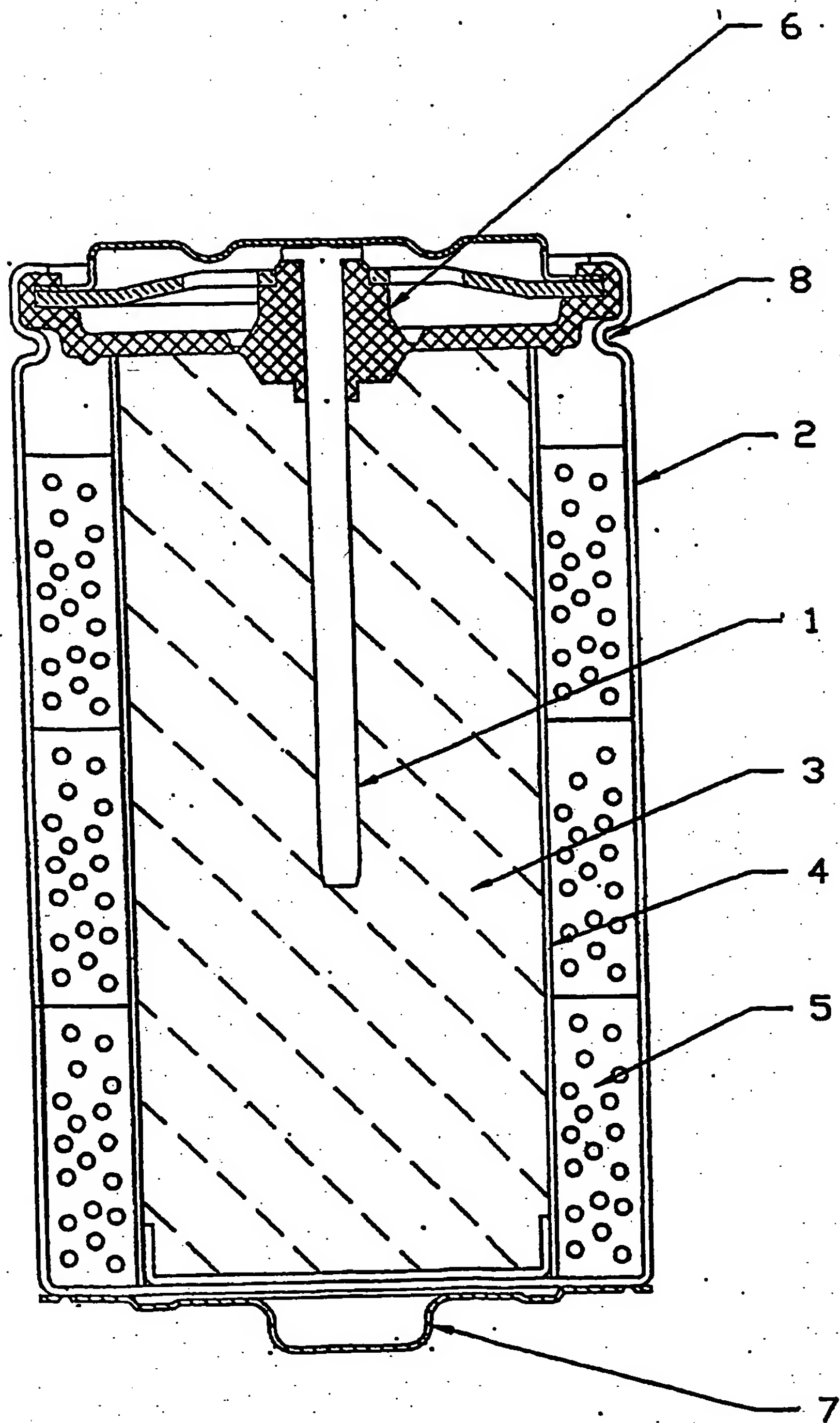


FIG 1

2/3

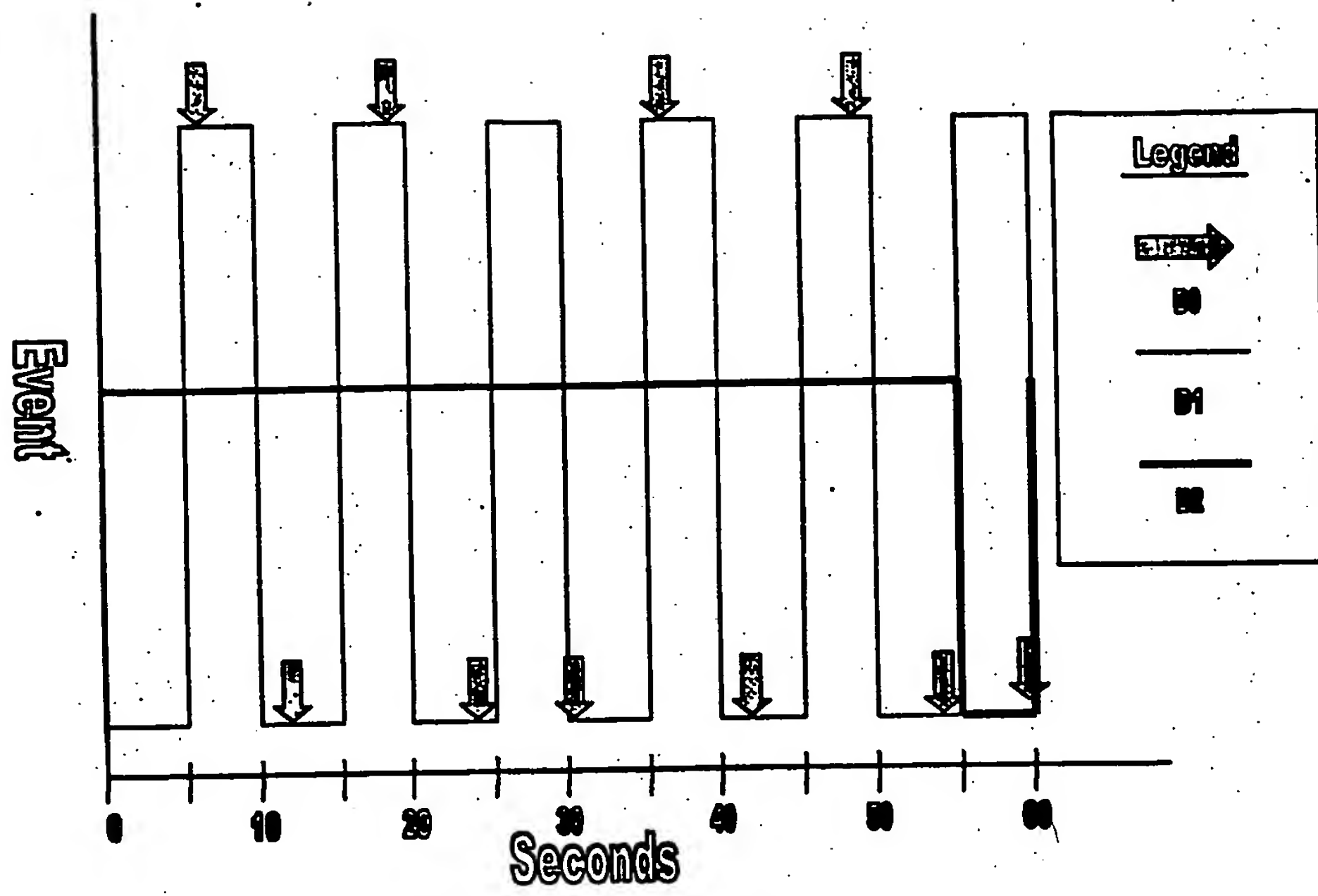


FIG 2

3/3

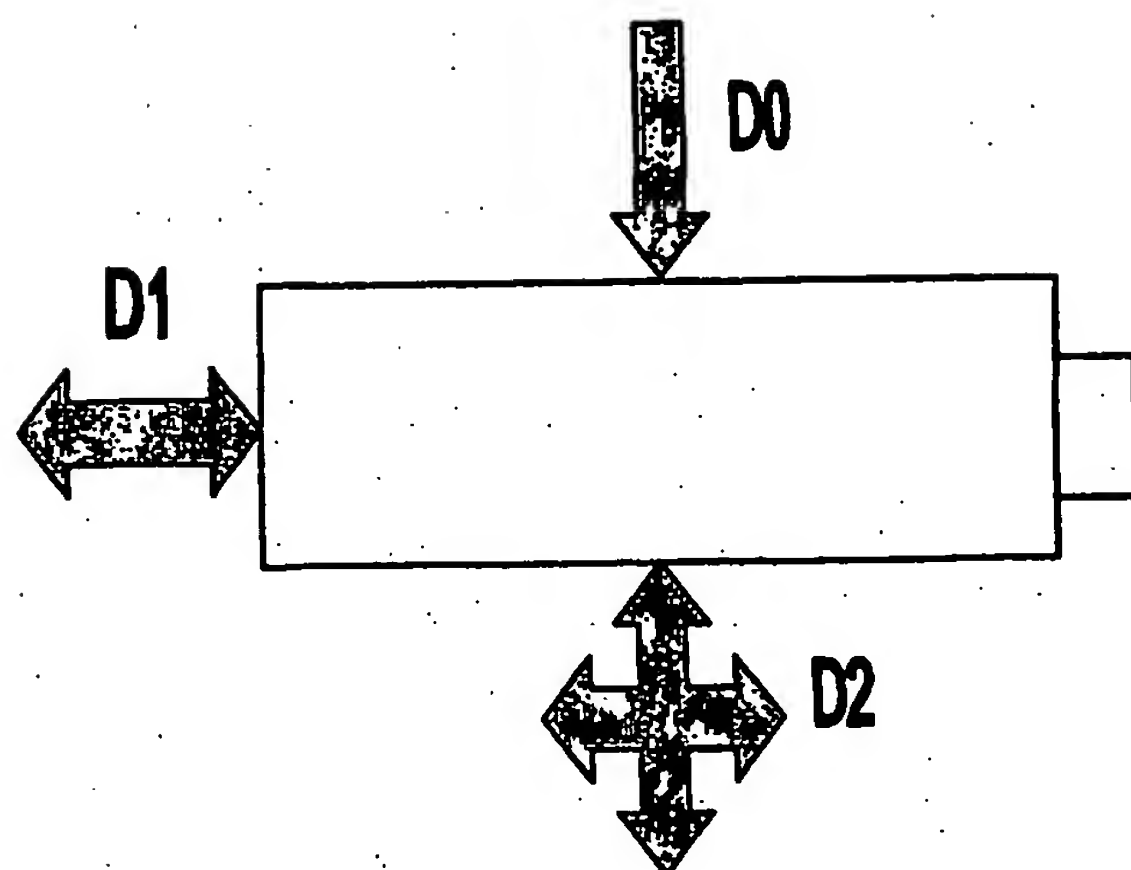


FIG 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/23495

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H01M 06/14

US CL : 429/300

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/300, 301, 302, 303

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,368,952 (SONNEVELD) 29 November 1994 (29.11.1994), column 10 lines 1-19	1-6, 22-26
X	US 4,315,976 (CONTE) 16 February 1982 (16.02.1982), column 3 lines 26-51.	1, 7-10, 24-26
X	US 4,260,669 (KERG) 7 April 1981 (07.04.1981), column 1 lines 7-31, column 3 lines 3-16, column 4 lines 32-46.	1, 2, 11-29

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

07 November 2001 (07.11.2001)

Date of mailing of the international search report

31 DEC 2001

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks

Box PCT

Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Mercedo, Julian

Telephone No. (703) 308-0661

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.